



## Evolution of electronic waste toxicity: Trends in innovation and regulation



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### ABSTRACT

Rapid innovation in printed circuit board, and the uncertainties surrounding quantification of the human and environmental health impacts of e-waste disposal have made it difficult to confirm the influence of evolving e-waste management strategies and regulatory policies on materials. To assess these influences, we analyzed hazardous chemicals in a market-representative set of Waste printed circuit boards (WPCBs, 1996–2010). We used standard leaching tests to characterize hazard potential and USEtox<sup>®</sup> to project impacts on human health and ecosystem. The results demonstrate that command-and-control regulations have had minimal impacts on WPCBs composition and toxicity risks; whereas technological innovation may have been influenced more by resource conservation, including a declining trend in the use of precious metals such as gold. WPCBs remain classified as hazardous under U.S. and California laws because of excessive toxic metals. Lead poses the most significant risk for cancers; zinc for non-cancer diseases; copper had the largest potential impact on ecosystem quality. Among organics, acenaphthylene, the largest risk for cancers; naphthalene for non-cancer diseases; pyrene has the highest potential for ecotoxicological impacts. These findings support the need for stronger enforcement of international policies and technology innovation to implement the strategy of design-for-the-environment and to encourage recovery, recycling, and reuse of WPCBs.

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### 1. Introduction

The accumulation, international transfers, and clandestine disposal of electronic waste (e-waste) is increasing worldwide because of technological innovation that shortens the useful lifespan of consumer electronic products (Ogunseitan and Shapiro, 2009). The annual generation of e-waste is estimated to be approximately 42 million tonnes per year (StEP, 2010), and there are two major concerns with the trend: the disposal of valuable resources, including rare earth metals where diminishing supplies could limit new production and innovation; and the risks to human health and environmental quality due to the hazardous constituents of untreated or poorly processed e-waste (Brian, 2013; Gordon et al., 2006; Hibbert and Ogunseitan, 2014). International regulations have been hardly effective in curbing the international flow, in part because of demand from artisanal miners of e-waste and the volatile prices of valuable metals in developing countries (NAB and SVTC, 2002; Ogunseitan and Schoenung, 2012). Printed circuit boards are

essential components of all the electrical and electronic equipment, where most of the valuable and potentially hazardous materials are concentrated. Recovery, dismantling, and recycling are considered among the most effective approaches to waste printed circuit boards (WPCBs) management, but large-scale implementation has been challenging because of projected low cost-to-benefit ratio of processing mixed e-waste components (Chen et al., 2013). Improved understanding of the chemical compositions of WPCBs has aided recyclers (Dervišević et al., 2013; Lee et al., 2012; Richter et al., 1997; Yin et al., 2011). For example, Yamane et al. (Luciana Harue et al., 2011) found that WPCBs from mobile phones (MPs) are composed of 63 wt.% metals; 24 wt.% ceramics and 13 wt.% polymers, while WPCBs from personal computers (PCs) are composed of 45 wt.% metals; 27 wt.% polymers and 28 wt.% ceramics. Meanwhile, copper in WPCBs from PCs was 20 wt.% and in WPCBs from MPs was 34.5 wt.%. However, these relative concentrations are sensitive to technological innovation, and it is not clear if regulation restricting hazardous components that have been shown to present risks to human health and the environment have also contributed as a driving force for change in materials use (Grant et al., 2013; Huabo et al., 2011; Ogunseitan, 2013; Quan et al., 2014; Song and Li, 2014a,b). For example, over the past 20 years, the central processing unit of computers has changed dramatically, and the improvement of electronic performance has also been accompanied by the use of new materials. Furthermore, international regulations, for

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example, the European Union's "Directive on Waste Electrical and Electronic Equipment" (WEEE) and "Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS, effective July 2006), were introduced to support the development of safer electronics by specifying maximum concentration limits for six restricted materials. Thus, we hypothesized that technological innovation and command-and-control regulations have independently and significantly changed the material resources value and chemical toxicity risk characteristics of WPCBs. There has been no reported study of the effect of technological innovation and regulatory policies on the sustainable resource and toxicity hazard characteristics of WPCBs.

To test the hypothesis, we collected WPCBs generated between 1996 and 2010, and we analyzed heavy metals and toxic organic chemicals to assess the influence of technological innovation in electronics manufacturing and toxic chemical regulatory policies. We conducted toxicity characteristic leaching assessments to determine whether the WPCBs are consistently classified as hazardous waste throughout the period studied (DTSC; U.S.E.P.A., 1992). We also used life cycle impact assessment model USEtox™ (<http://www.usetox.org>, version 1.1) to investigate changes in the potential environmental and human health impacts of WPCB disposal across the sampling period (Hauschild et al., 2008; Huijbregts, 2010). We expect that the results of this study will give valuable information on the roles of technological innovation and command-and-control regulation in resource conservation and in reducing the use of toxic materials in ubiquitous consumer products such as electronics.

## 2. Materials and methods

### 2.1. Sample collection and preparation

Fourteen intact WPCBs generated annually from 1996 to 2010 (except 2001) originating from computers were used for the study. Detailed information about the samples is presented in Supporting Information Table A. The brand of WPCBs consisted mainly of Asus brand and these samples were mainly produced in Mainland China and Taiwan. The physical dimensions (length and width) were in the range of 23.5–30.5 cm and 17–24.5 cm, respectively. The weight range was 387.7–669.1 g. Five different digital memory technologies, EDO/DRAM, SDRAM, DDR, DDR2 and DDR3, were represented in the samples, according to the dominant technology during each timeframe of PCB production. The Central Processing Units (CPUs) represented were Intel and AMD. Based on chipset characteristics, we divided the samples into categories of Intel and non-Intel processors. Intel chipset were further organized into three sub-categories: Intel 400, 800 and 900 series.

Before chemical analyses, all the samples were shredded to 20 × 20 mm pieces by an investigator-designed machine, and then crushed by a cutting mill (SM-2000, Retsch, Germany) to around 9.5 mm as required by Toxicity Characteristic Leaching Procedure (TCLP) (U.S.E.P.A., 1992). After that, each batch was further powdered to 2.0 mm for Waste Extraction Test (WET) and 1.0 mm for Total Threshold Limit Concentration (TTL) after homogenization and partition (DTSC).

### 2.2. Chemical leaching assessment procedures

Three standard procedures, TCLP (Method 1311; 40 CFR §261.24), WET and TTL (California Department of Toxic Substances Control, DTSC; Title 22) were used to evaluate the solid waste classification of WPCBs. According to the TCLP procedure, eight metals, As, Ba, Cd, Cr, Pb, Hg, Se and Ag, were analyzed. For TTL, 24 metals were examined: Ag, Al, As, Au, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Li, Mg, Mo, Ni, Pb, Pd, Sb, Se, Sn, Ti, V, Zn. For TTL, if the total concentration in the waste extract of any regulated metal equalled or exceeded the Soluble Threshold Limit Concentration (STLC; 19), then those metals were further analyzed by WET.

For TCLP or WET, 10 g of shredded WPCBs was placed into an extraction vessel, which was then placed in a rotary extractor for the specified time period (18 h for TCLP and 48 h for WET). Then the resulting suspension was filtered through a 0.45 μm glass fiber filter. For TTL, 1 g of 2 mm particles was added to a 250 mL vessel, then extracted by repeated additions of HNO<sub>3</sub>, followed by a 30% H<sub>2</sub>O<sub>2</sub> solution in water, as specified by EPA Method 3050B. The leachate was then filtered through a 0.45 μm filter and diluted to 50 mL. Finally the leachate was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 5300DV).

### 2.3. Toxic organic pollutants

Polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs, mono- to deca-BB, PBB-1 to PBB-10), polybrominated diphenyl ethers (PBDEs, mono- to deca-BDE, PBDE-1 to PBDE-10), sixteen Poly-aromatic hydrocarbon compounds (PAHs) on US EPA's priority list [Naphthalene (Nap), Acenaphthylene (AcPy), Acenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Benz[a]anthracene (BaA), Chrysene (CHR), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (IP), Dibenzo[a,h]anthracene (DA), Benzo[g,h,i]perylene (BP)] and Tetrabromobisphenol A (TBBPA) were all examined. Details about the analytical procedures are provided in the Supporting Information.

Chemical reagents used are HPLC grade or equal to this grade. For quality control purposes, a Calibration Blank (CB), Laboratory Control Standard (LCS), Method Blank (MB), Sample and Duplicate, and Matrix Spike were analyzed for each batch, and a Mid-Range Calibration Verification Standard (MRCVS) and Calibration Blank (CB) were analyzed each 10 injections. Additionally, a duplicate sample was processed and analyzed to assess the variability of the procedures.

### 2.4. Life cycle impact assessment by USEtox™

USEtox™ is a standardized environmental model, developed by collaboration of the United Nations Environment Program (UNEP) and the Society for Environmental Toxicology and Chemistry (SETAC). Ecotoxicity and human toxicity, both carcinogenic impacts and non-carcinogenic impacts, for each metal and organic substance were calculated based on the following formula (Hauschild et al., 2008; Huijbregts, 2010):

$$IS = \sum_i \sum_x CF_{x,i} M_{x,i} \quad (1)$$

where *IS* represents the impact score for e.g. human toxicity (cases); *CF<sub>x,i</sub>* the characterization of substance *x* released to compartment *i* (cases/kg) and *M<sub>x,i</sub>* the emission of *x* to compartment *i* (kg). The unit of the characterization factor for ecotoxicity is PAF m<sup>3</sup>day/kg<sub>emission</sub> and for human toxicity cases/kg<sub>emission</sub> both summarized as Comparative Toxic Unit (CTU).

## 3. Results and discussion

### 3.1. Metallic contents of WPCBs

The results of Total Threshold Limit Concentrations assessment (Table 1) indicated that the most abundant metal contained in the WPCBs is copper (ranging from 177 000 to 268 000 mg/kg), which is at least an order of magnitude higher than other metals in the WPCBs, accounting for approximately 51% of the total metallic content. Copper is used to transmit electric signals in the PCBs (Duan et al., 2011), and its use is fundamental, regardless of technological innovation or period of PCB manufacture. Iron (142 00–149 000 mg/kg), aluminum (295 00–816 00 mg/kg), tin (393 00–648 00 mg/kg) and zinc (190 00–552 00 mg/kg) are also abundant, together representing

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